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THE IONIZATION POTENTIAL OF SELENIUM VAPOR

BY
A. D. UDDEN

A THESIS
PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

Reprinted from THE PHYSICAL REVIEW, N. S., Vol. XVIII, No. 5, November, 1921.

Diss.
Philadelphia
1921.

87803

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Synopsis.

Ionization potential of selenium vapor was determined from current potential curves obtained with a four electrode, pyrex glass tube. Nickel was used for the electrodes. After the cleaning out process the selenium was spilled into the bottom of the tube and vaporized by means of an oil bath kept at 168 to 282° C. Both total negative current measurements were made and positive current measurements according to the Lenard method, and corrections were applied for the potential fall along the electrically heated salted platinum cathode and for the initial energy of the electrons. The ionization potential comes out 12.7 ± 0.4 volts. Putting this value in the quantum equation we get 980 Å as the short wave-length limit of the selenium spectrum.

THE ionization and resonance potentials of several elements belonging to group VI. of the periodic table have already been determined.[1] In continuation of the study of the elements of this group, this paper presents the results of a determination of the ionization potential of selenium vapor.

The significance of critical potential determinations has frequently been pointed out. When an electron possesses a certain critical speed it is capable of ionizing a given vapor atom by collision. That potential which can impart this speed to an electron is known as the ionization potential of the given vapor. According to Bohr's theory, if the ionization potential V of a vapor has been determined, the limiting frequency ν of the spectrum of this vapor may then be calculated from Planck's formula, $\nu = Ve/h$.

The ionization potential of selenium vapor was obtained by the usual method of accelerating the electrons from a hot filament to metal electrodes to which suitable potentials were applied. Current potential curves were plotted and the ionizing potential was indicated by an abrupt change of curvature in each of the graphs. Corrections were applied for the drop in potential along the filament and for initial velocity of emission of the electrons. The initial velocity correction was made by applying back potentials on the grid just sufficient to stop the electron current.

A diagram of the apparatus used in the present investigation is shown in Fig. 1. The pyrex glass tube was made in two sections, ground to a

[1] Scientific Papers of the Bureau of Standards, No. 400.

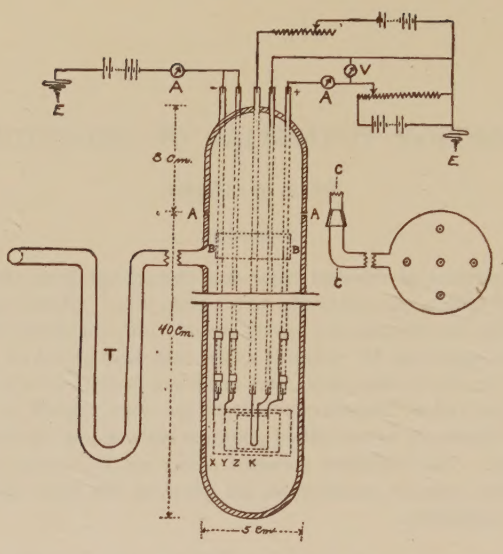

Fig. 1.

smooth fit at *A–A*, and these were sealed together with DeKhotinsky cement. The nickel plate *X* and the grids *Y* and *Z* were cylindrical in shape and placed coaxially with reference to the cathode *K*. The electrodes were held in place by means of clasps fitting on slender pyrex tubes sealed into the upper section of the large tube. A small mica cup at *B–B* contained the selenium which was to be vaporized. The cathode consisted of a thin strip of platinum coated with several applications of barium and strontium oxides. When measurements were being made a freezing mixture of carbon dioxide snow surrounded the trap *T*.

With proper heat treatment of the tube and the electrodes a vacuum of about .003 millimeter pressure was obtained, after which the selenium was spilled into the bottom of the tube by rotating the latter about a horizontal axis *C–C*. The selenium was then vaporized by means of an oil bath surrounding the lower part of the tube. Some difficulty was experienced in finding a metal suitable for use as electrodes in the vapor. Copper was attacked by the vapor and a polarizing layer appeared to form on the surface of iron. A white powder formed on the nickel electrodes but this did not seriously interfere with the flow of electron currents.

The ionization potential was determined by both total current and positive current measurements. In the case of total current measurements, the plate and two grids were connected together so as to form a single electrode to which positive accelerating potentials were applied.

For the positive current or Lenard method the electrodes were connected as shown in the diagram. In the latter case a negative potential of about 15 volts was applied to the outer electrode.

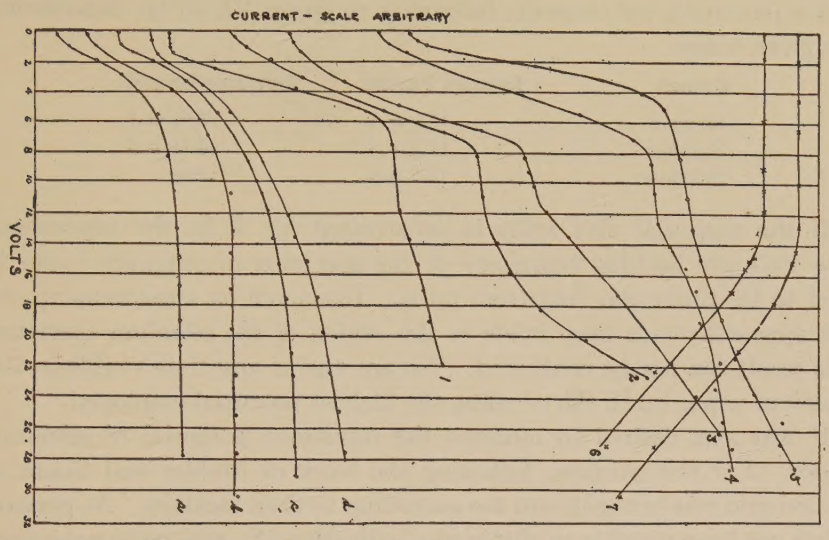

Fig. 2.

Runs were first made without the selenium vapor, keeping the conditions otherwise the same as when the vapor was present in the tube. Curves such as *a*, *b*, *c* and *d* (Fig. 2) were then obtained. It will be noticed that these curves flat off quite regularly and do not show any sudden increase in the electron current. Curves 1, 2, 3, 4, 5, 6 and 7 were made with vaporized selenium present in the tube, the temperature of the vapor varying from 168 to 282 degrees Centigrade for the different runs. Graphs 1 to 5 are total current measurements while 6 and 7 were obtained by the Lenard method. The graphs as plotted include the corrections for potential drop along the filament, the corrections varying from 1.0 to 2.4 volts. The initial velocity corrections are shown in the accompanying table. In some cases the temperature of the filament was so low that no appreciable initial velocity was obtained.

No. of Curve.	Break, Volts.	Initial Velocity, Volts.	Ionization Potential, Volts.	Deviation from Mean.
1	12.0	—	12.0	−.7
2	11.8	1.5	13.3	+.6
3	11.6	.5	12.1	−.6
4	12.7	.1	12.8	+.1
5	13.0	—	13.0	+.3
6	12.5	.1	12.6	−.1
7	13.0	—	13.0	+.3

The average ionization potential of selenium vapor calculated from these measurements is 12.7 ± .4 volts. This is quite close to the value obtained for sulphur by Mohler and Foote.[1] The ionization and resonance potentials for elements belonging to group VI. so far determined are given below.

Element.	Ionization Potential.	Resonance Potential.
Oxygen	155. ± .5	7.91 ± .1
Sulphur	12.2 ± .5	4.78 ± .5
Selenium	12.7 ± .4	——

If the potential 12.7 volts is substituted for V in the expression, $\nu = Ve/h$ the limiting frequency of the spectrum of selenium vapor is seen to be about 980 Ångstrom units. Inasmuch as measurements do not appear to have been made in this region of the selenium spectrum this result can not be confirmed. No arc was at any time visible in the selenium vapor up to thirty volts, the highest potential employed.

It was also desired to measure the resonance potential of selenium vapor. For this purpose, following the work of Mohler and Foote, a second grid was brought into use according to their method. At present it has not been possible to obtain any indication of a resonance potential. With further modifications of the dimensions and distances separating the electrodes it is possible that a resonance potential may be determined. This might provide a more satisfactory correction for the initial velocity of emission of the electrons.

The writer is under obligations to Dr. C. B. Bazzoni for suggestions and advice received during the course of the work upon this experiment

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